

Vibrationally-Resolved Sum-Frequency Generation with Broad-Bandwidth Infrared Pulses

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Abstract

We present a novel procedure for vibrationally-resolved sum-frequency generation (SFG) in which a broad-bandwidth IR pulse is mixed with a narrow-bandwidth visible pulse. The resultant SFG spectrum is dispersed with a spectrograph and detected in parallel with a scientific grade CCD detector, enabling rapid and high signal to noise data acquisition over a 400 cm⁻¹ spectral region without scanning the IR frequency. Application to the study of a self-assembled monolayer of octadecanethiol is discussed.

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Vibrationally-resolved sum-frequency generation (SFG) spectroscopy, initially demonstrated by Shen and coworkers,¹ is a powerful probe of the molecular order at surfaces and interfaces.² In most SFG studies, a narrow-bandwidth IR pulse mixes with a narrow-bandwidth visible pulse through a $\chi^{(2)}$ process at an interface to produce SFG that is not spectrally analyzed. The sum frequency (SF) spectrum is laboriously acquired by scanning the wavelength of the IR pulse over the vibrational resonances. In this letter, we describe an alternate approach that obtains SFG spectra with short acquisition times and without wavelength tuning. A nominally 100 fs laser system generates broad-bandwidth (BB) IR pulses that are mixed with narrow-bandwidth visible pulses at the interface of interest. The SF light is collected and dispersed in a spectrograph. A scientific grade CCD detector is used to detect all of the SF light (spectral range: 600 cm⁻¹) in parallel. The spectral resolution of this approach is determined by the spectrograph and the bandwidth of the nonresonant visible pulse. This BB SFG approach, using a table-top commercial laser system, rapidly produces excellent spectra, and in principle, permits ultrafast time resolution.

Figure 1 details the optical system based on an optical parametric amplifier (OPA) pumped at 1 kHz repetition rate by a Ti-sapphire regenerative amplifier^{3,4} that produces 800 nm pulses with 100 fs full-width at half-maximum (FWHM) duration,⁵ 12 nm FWHM bandwidth, and >800 μ J energy. In the OPA, a 2-pass type-II BBO crystal seeded by a white-light continuum produces signal and idler pulses with combined energy >220 μ J. The OPA tunes with nearly constant combined power over the range of signal wavelengths from 1200 nm to 1600 nm. Autocorrelation of the signal at 1311 nm indicates pulses with

100 fs FWHM. The signal and idler bandwidths are 43 nm at 1311 nm and 110 nm at 2091 nm, respectively. The pulse-to-pulse stability of the total OPA energy is 5%.⁶

Broad-bandwidth, tunable IR pulses are generated by difference frequency (DF) mixing the signal and idler of the OPA in a 2 mm AgGaS₂ crystal that is $\lambda/4$ AR coated on input at 1.6 μm and on output at 5.0 μm . The scheme is comparable to that of Ref. 7. The orthogonally polarized signal and idler pulses are separated by a dichroic mirror (BS in Fig. 1), re-timed for optimal overlap, and combined colinearly on a second dichroic mirror. The beams are unfocused and a near IR camera measured the spatial profile of the signal at the DF crystal to be 2.8 mm x 3.4 mm.⁸ The signal and idler pulses are separated from the IR with a dichroic long pass filter. 180 μJ combined signal and idler onto the DF crystal produce 6 μJ pulses at 3.4 μm , with a FWHM bandwidth of 0.3 μm (250 cm^{-1}) and pulse duration of about 0.22 ps FWHM (measured by autocorrelation). As the OPA and DF crystals are tuned, the IR pulse energy is $> 3 \mu\text{J}$ from 3 μm to 8 μm (the long wavelength cut-off of our IR spectrometer). The pulse-to-pulse stability of the IR energy is 9%.

We explored several ways to produce narrow-bandwidth visible pulses for the SFG. The most successful to date is diagramed in Fig. 1. After 2 passes through the 4 pass compressor, the amplified 800 nm pulses are spectrally dispersed and about 100 ps long; the blue edge of the pulse is stripped from the beam with mirror M1. The removal of 80 μJ of amplified light produces a slight (linear) decrease in the OPA energy. This stripped beam is both spatially and temporally chirped. However, the area of the stripped beam is comparable to the spot size of the collimated beam that first strikes the grating, and the spatial chirp is pseudo scrambled. The bandwidth of the stripped beam is 50 cm^{-1} FWHM and the measured frequency chirp is approximately 1.8 cm^{-1} per ps. A home-built, 46 cm focal length (FL), symmetric Czerny-Turner monochromator with a 1740 gr/mm grating provides a variable reduction in bandwidth and partially compensates for the remaining temporal chirp on the beam. The duration of the 795 nm output of the monochromator (75% energy efficient) is 7 ps FWHM for bandwidths between 2.5 cm^{-1} and 20 cm^{-1} FWHM, and the pulse energy is nominally linear in bandwidth.

The visible and IR pulses are polarization selected, brought to temporal and spatial overlap on a dichroic mirror (BC in Fig. 1) and focused with a simple 10 cm FL CaF₂ lens onto the sample at an incidence angle of 45°. As the lens is not an achromat, the IR focus is 4 mm beyond the 795 nm focus. In the SFG experiments, the sample is positioned beyond the 795 nm focus to avoid sample damage by the visible beam. The areas of the visible and IR spots at the sample were approximately 10⁻⁴ cm² and 4x10⁻⁵ cm² respectively. Typical operating conditions, set by transport losses and inefficiency in the combining mirror, are 3 μJ and 4 μJ for 3.4 μm and 795 nm pulses at the sample, with FWHM bandwidths of 250 cm^{-1} and 4.8 cm^{-1} respectively.

The reflected beams from the sample are recollimated with a 10 cm FL lens. The 795 nm light is blocked by three dichroic mirrors (standard 800 nm high reflectors); the SFG is polarization analyzed and then focused by a 10 cm FL lens into a 0.75 m spectrograph with a 1200 gr/mm grating. The SF light is dispersed across a liquid-nitrogen-cooled,

backthinned, scientific-grade CCD detector.⁹ The CCD array is 330(V) x 1100(H, dispersing direction) pixels with a pixel size of 24 μm . Because it is focused through the entrance slit, the SFG typically covers only a few pixels in the vertical direction, which are binned during the data collection. The dispersion of the spectrograph at the SF (nominally 645 nm), is 0.023 nm (0.56 cm^{-1}) per bin; the inherent resolution of the spectrograph/array is 2 bins.

Shown in Fig. 2 are BB SFG spectra for a self-assembled monolayer (SAM) of (a) fully deuterated octadecanethiol (d-ODT) and (b) fully hydrogenated octadecanethiol (ODT) on a Au film, using IR spanning the C-H stretch vibrational resonances. The spectra were acquired with p-polarized visible, IR and SF beams. The acquisition time for each spectrum was 60 s. Observed spectral widths of SFG vibrational resonances were the same using 795 nm bandwidths of 2.0 cm^{-1} and 4.8 cm^{-1} ; broadening was observed at bandwidths $\geq 6\text{ cm}^{-1}$. Peak signals typically correspond to about 350 detected photons per second per (0.56 cm^{-1}) bin. The high frequency “hash” on the ODT and d-ODT spectra is not random noise but a recurrent etalon-type fringe pattern with 10 pixel spacing. Since a fully deuterated SAM has no vibrational resonances in this spectral region, one may ratio the SFG spectrum of ODT to the SFG spectrum of d-ODT to account for the IR spectrum. As is shown in Fig. 2c, this normalization removes most of the etalon interference. The SF resonances show a derivative-like lineshape due to the interference between the resonant SAM response and the nonresonant Au response.²

The alkane chains of perfectly ordered ODT SAMs on gold are in a *trans*-extended configuration. CH_2 modes of all-*trans* alkane chains are symmetry forbidden in SFG, so only the terminal methyl resonances should be observed. The three prominent features seen in the SFG spectra of the ODT monolayer are in agreement with spectra in the literature¹⁰ and can be assigned to the $\text{CH}_3\text{ v}_s$ at 2877 cm^{-1} , the $\text{CH}_3\text{ v}_{\text{asy}}$ at 2964 cm^{-1} , and a Fermi resonance between the $\text{CH}_3\text{ v}_s$ and a CH_3 bend overtone at 2937 cm^{-1} . Methylene resonances are present in figure 2c as a small peak at 2850 cm^{-1} , assigned to the $\text{CH}_2\text{ v}_s$, and a broad band in the region 2890 cm^{-1} to 2930 cm^{-1} , attributable to either the $\text{CH}_2\text{ v}_{\text{asy}}$ and/or a Fermi resonance between the $\text{CH}_2\text{ v}_s$ and CH_2 bend overtones. The observation of methylene resonances indicates some disorder in this SAM from the all-*trans* configuration. The ability to detect and resolve the weak methylene resonances demonstrates the excellent signal-to-noise and spectral resolution of our approach.

The BB SFG spectra are of remarkably good quality given the rapid acquisition time. Spectra of comparable quality have been obtained in the C-D stretch region ($2200\text{--}2000\text{ cm}^{-1}$) for deuterated SAMs. Note that no pulse-to-pulse normalization of the spectra has been made. As the entire spectrum is recorded on each laser shot, the system is quite insensitive to amplitude fluctuations. Since no tuning of the IR or visible pulses occurs during spectral acquisition, the problem of maintaining constant spatial overlap while scanning is obviated. We obtained BB SFG spectra over the tuning range of $3\text{ }\mu\text{m}$ to $8\text{ }\mu\text{m}$. In an experiment somewhat similar to ours, van der Ham *et al.* used the self-dispersive nature of non-collinear SFG to record (on a CCD array) spectra of thiophenol on Ag in the wavelength range $9.9\text{ }\mu\text{m}$ – $10.8\text{ }\mu\text{m}$, using moderate bandwidth (25 cm^{-1} FWHM) IR light

from a free-electron-laser.¹¹ The present ultrafast source with spectrograph-dispersed SFG produces spectra over a much wider bandwidth.

As the stripped 795 nm beam has nominally constant power-per-unit-bandwidth over the central 40 cm^{-1} , the pulse energy, and hence the SFG signal, can be increased by opening the monochromator exit slit to obtain the best balance between signal intensity and spectral resolution. In principle, the SFG signal amplitude will increase until the visible bandwidth becomes comparable to the natural linewidth of the sample, after which both the apparent width of the SF resonance and the integrated signal will increase. In practice, the relationship between the bandwidth of the visible pulse and the resolution of the SFG spectrum is simple only when the visible bandwidth is narrow or nearly transform limited.

Two other ways of generating visible mixing pulses were successfully tried. In one, the beam stripped from the compressor was sent directly to the sample (no bandwidth-limiting monochromator). Although approximately 50 cm^{-1} broad, the stripped beam was stretched in time (chirped 1.8 cm^{-1}/ps). Only the frequencies of the visible spectrum at the sample during IR pulse, or within the dephasing time T_2 (the vibrational resonance FWHM $\Delta\nu=(\pi T_2)^{-1}$; for $\Delta\nu=10.6 \text{ cm}^{-1}$, $T_2=1.0 \text{ ps}$), contribute to the width of the SFG. Although SFG spectra with resolution and signal to noise similar to Fig. 2 were obtained with this approach, it has two disadvantages. More visible light strikes the sample than contributes to the SFG signal, and the excess may cause sample damage. Also, the absolute frequency of the SFG vibrational features can vary within the 50 cm^{-1} envelope of the visible pulse, depending on alignment (timing) with respect to the IR; it was always necessary to use an absolute IR frequency reference (absorption cell with HCl gas) with this approach. Alternatively, the residual 800 nm pulses from the OPA (250 cm^{-1} FWHM, 500 μJ not converted to signal and idler) were used. Before going to the sample, the 0.15 ps pulses were stretched with a double-grating delay line; the chirp was controlled by varying the distance between the two grating passes. As with the preceding setup, the chirp determined the effective 800 nm bandwidth. Again, spectra similar to Fig. 2 were obtained. In addition to the two problems mentioned above, this approach has the disadvantage that the spectrum of the residual 800 nm is strongly coupled to the operation of the OPA, and may be severely distorted by nonlinear processes in the BBO crystal.

In conclusion, the method presented here for broad-bandwidth sum-frequency generation and parallel multichannel detection offers very fast data acquisition with high signal-to-noise-ratio. Since complete spectral information is obtained on every laser shot, the method should be particularly useful for time resolved studies. One example is ultrafast pump/probe experiments of vibrational dynamics at surfaces, where the time resolution would be determined by the IR pulse duration (which could presumably be compressed to less than the present 0.2 ps). Another use is the study of phase transitions of films induced by changes in surface pressure or temperature, where it is useful to obtain complete spectra rapidly as P or T is being ramped through the transition region.

References

- ¹ J.H. Hunt, P. Guyot-Sionnest, and Y.R. Shen, Chem. Phys. Lett. **133**, 189 (1987); P. Guyot-Sionnest, J.H. Hunt, and Y.R. Shen, Phys. Rev. Lett. **59**, 1597 (1988).
- ² Y.R. Shen, Nature **337**, 519-525 (1989); C.D. Bain, J. Chem. Soc. Faraday Trans. **91**, 1281 (1995); G.L. Richmond, Anal. Chem. **69**, A536 (1997).
- ³ Clark MXR IR-OPA and CPA1000.
- ⁴ Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
- ⁵ A Gaussian temporal shape was assumed to deconvolute all autocorrelation and crosscorrelation measurements.
- ⁶ All reported stability measurements are 2σ based on 1000 shot averages.
- ⁷ F. Seifert, V. Petrov, and M. Woerner, Opt. Lett. **19**, 2009 (1994).
- ⁸ All reported beam dimensions are $1/e^2$ intensity diameters.
- ⁹ Princeton Instruments LN/CCD-1100PB detector with ST 138 controller.
- ¹⁰ A.L. Harris, C.E.D. Chidsey, N.J. Levinos, and D.N. Loiacono, Chem. Phys. Lett. **141**, 350 (1987); C.D. Bain, P.B. Davies, T. Hui Ong, R.N. Ward, and M.A. Brown, Langmuir **7**, 1563 (1991); M.A. Hines, J.A. Todd, and P. Guyot-Sionnest, Langmuir **11**, 493 (1995); M.S. Yeganeh, S.M. Dougal, R.S. Polizzotti, and P. Rabinowitz, Phys. Rev. Lett. **74**, 1811 (1995).
- ¹¹ E.W.M. van der Ham, Q.H.F. Vreken, E.R. Eliel, Opt. Lett. **21**, 1448 (1996).

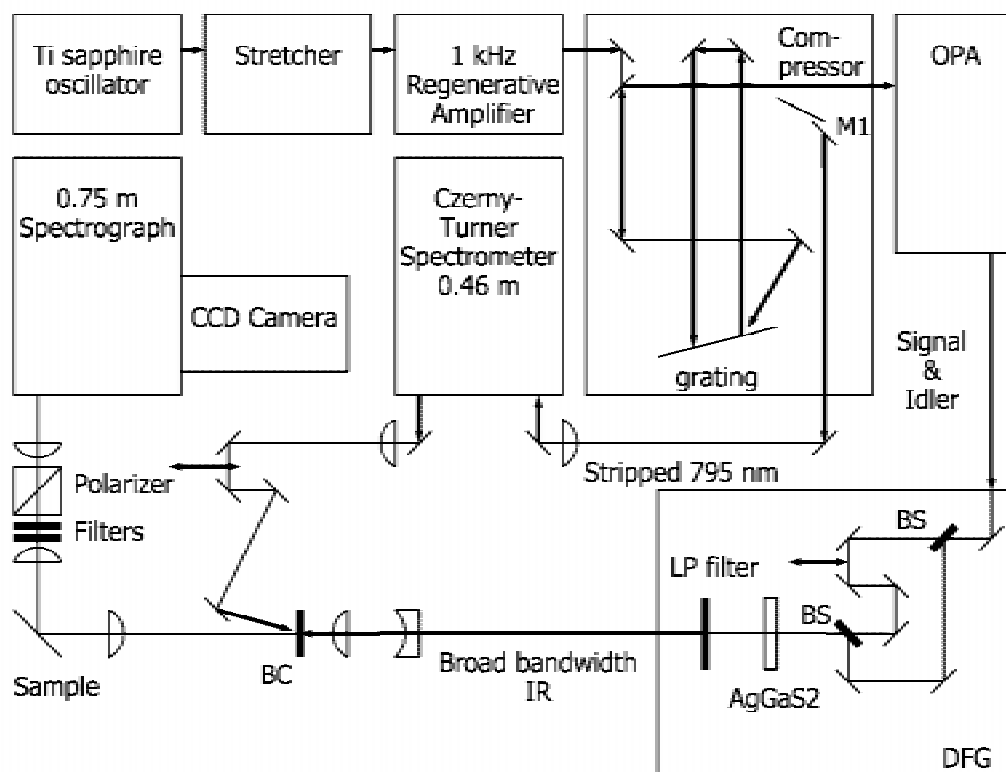


Fig. 1. Schematic diagram of the optical system. See text for details.

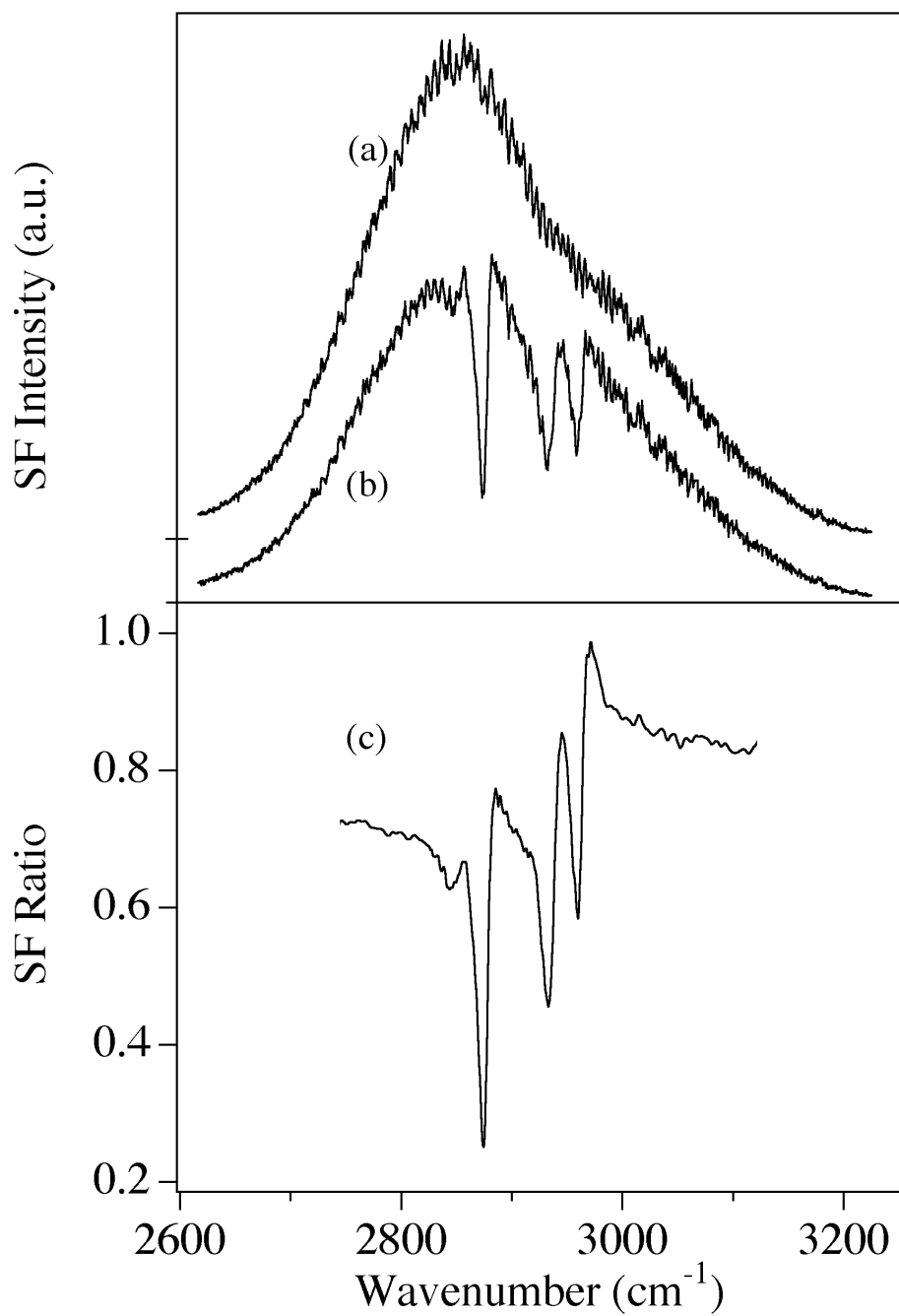


Fig. 2. SFG spectrum of an Au film covered with (a) a self-assembled monolayer of d-ODT and (b) a self-assembled monolayer of ODT, and (c) the ratio b/a. The spectra were recorded in 60 s with p-polarized IR and visible incident beams, and p-polarized detection of the SF. The visible bandwidth was 4.8 cm^{-1} . Traces (a) and (b) are offset vertically; a line indicating zero signal is shown for each.